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C08G 61/00 // C09K 11/06

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U1S S1411 S1927

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US 5121029 A US 5069975 A

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Online databases: WPI, CLAIMS, CAS ONLINE

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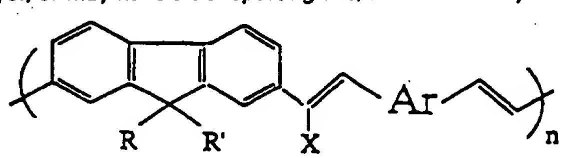
United Kingdom

(54) **Fluorene-based alternating copolymers and electroluminescence elements**

(57) Fluorene-based alternating copolymers to be used as light emitting materials of electroluminescent elements have the following formula (I). Electroluminescent elements may have an anode/luminescent layer/cathode structure, in which the fluorene-based alternating copolymer is used as light emitting materials of the luminescent layer, or may have a transporting and/or reflection layer added thereto, if necessary.

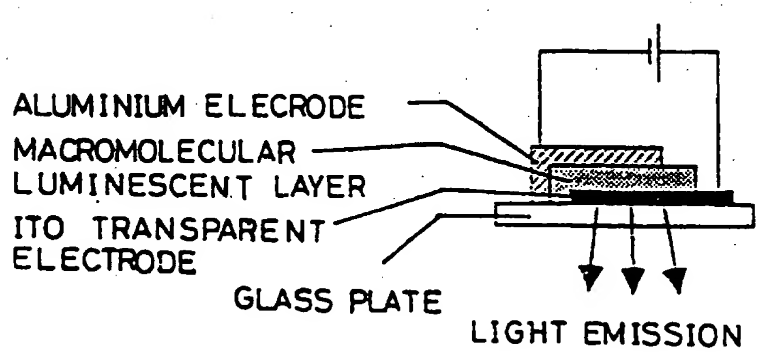


(I)

where

R and R' are each H, alkyl, cycloalkyl, aryl, alkoxy, cyclalkoxy or aryloxy
X is H or CN
Ar is alkylene or arylene, optionally substituted.

FIG. 9



GB 2 313 127 A

FIG. 1

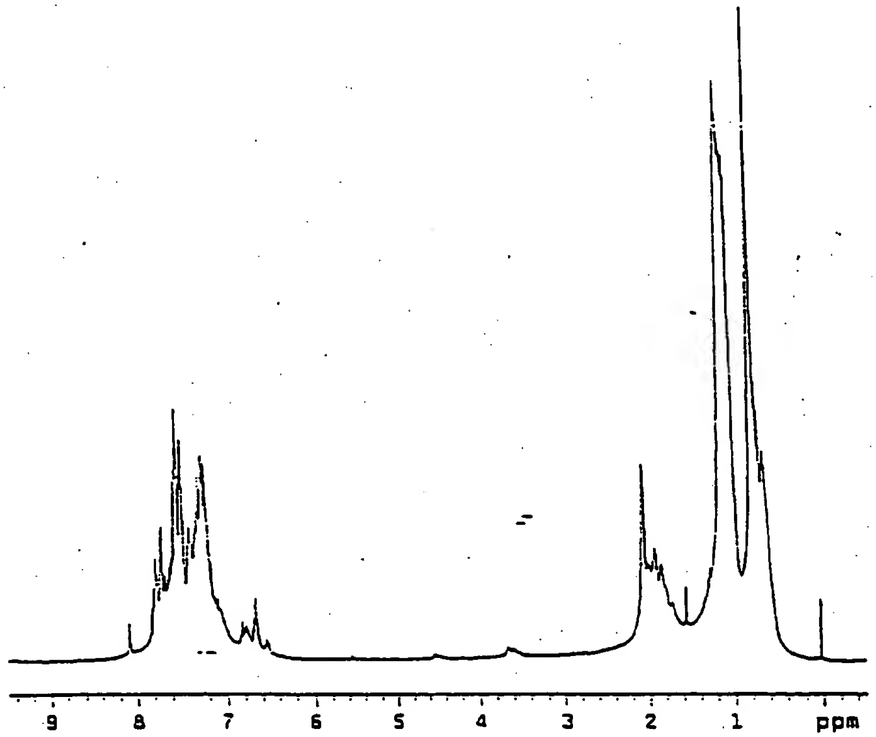


FIG. 2

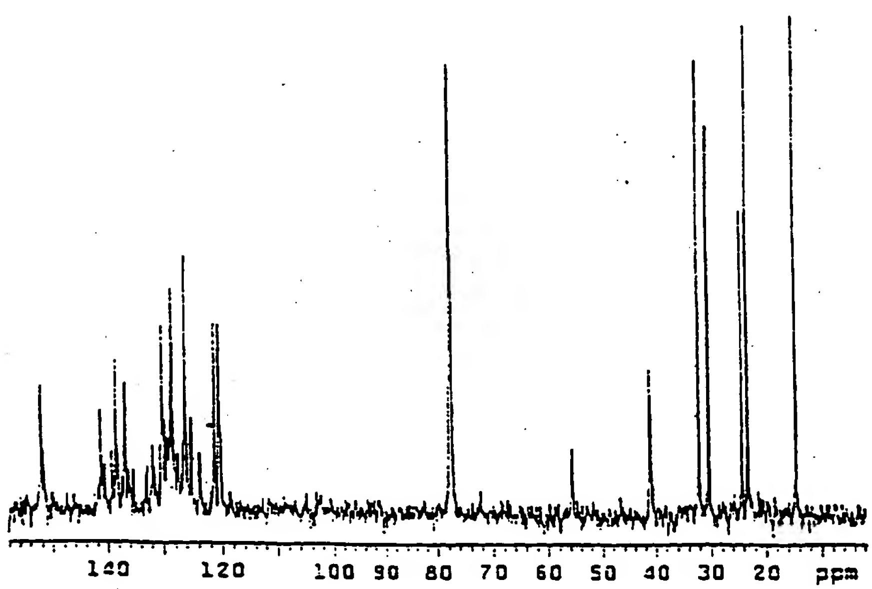


FIG.3-1

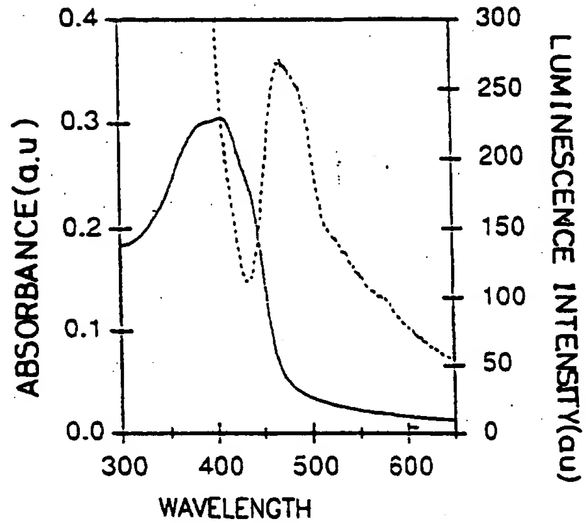

0.4
0.3
0.2
0.1
0.0
300
400
500
600
WAVELENGTH
ABSORBANCE(a.u)
300
250
200
150
100
50
0
LUMINESCENCE INTENSITY(a.u)

FIG.3-2

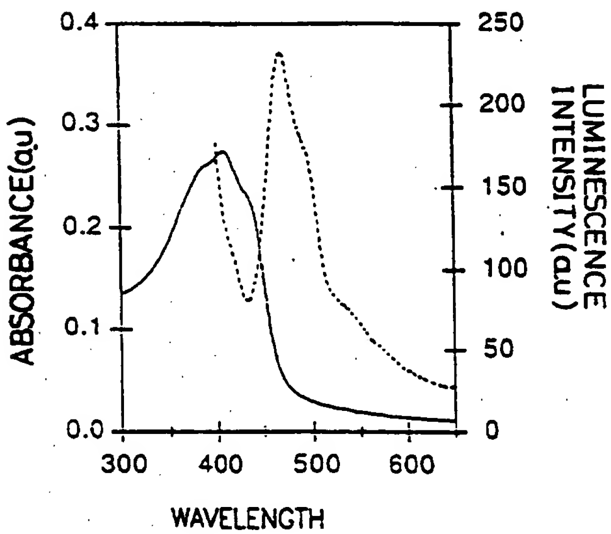

0.4
0.3
0.2
0.1
0.0
300
400
500
600
WAVELENGTH
ABSORBANCE(a.u)
250
200
150
100
50
0
LUMINESCENCE INTENSITY(a.u)

FIG.3-3

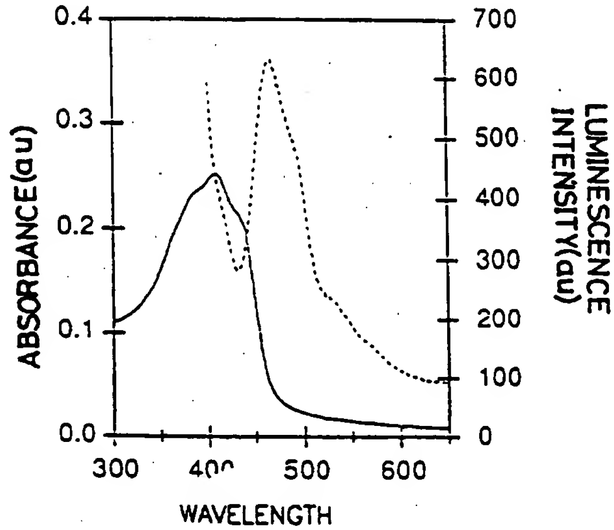

0.4
0.3
0.2
0.1
0.0
ABSORBANCE(au)
700
600
500
400
300
200
100
0
LUMINESCENCE INTENSITY(au)
300
500
600
WAVELENGTH

FIG.3-4

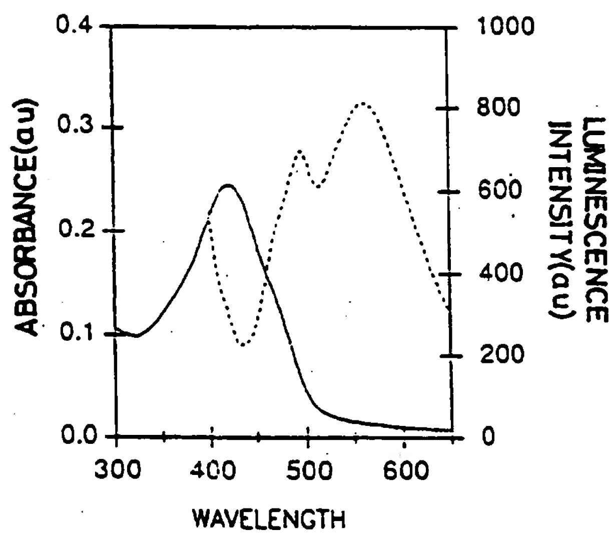

0.4
0.3
0.2
0.1
0.0
ABSORBANCE(au)
1000
800
600
400
200
0
LUMINESCENCE INTENSITY(au)
300
400
500
600
WAVELENGTH

FIG.3-5

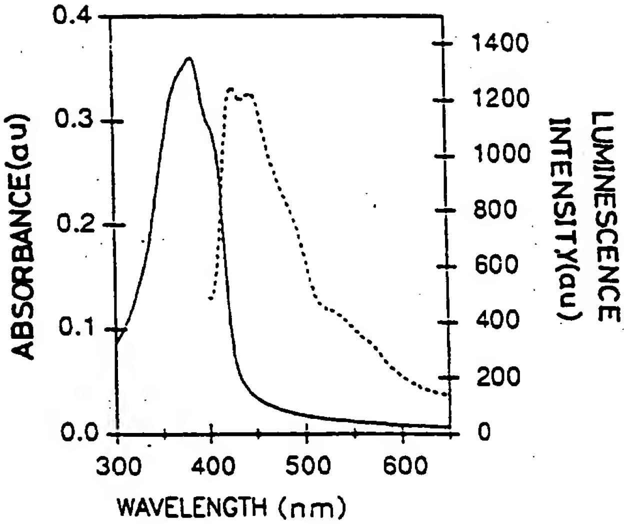

0.4
0.3
0.2
0.1
0.0
ABSORBANCE(au)
1400
1200
1000
800
600
400
200
0
LUMINESCENCE INTENSITY(au)
300
400
500
600
WAVELENGTH (nm)

FIG.3-6

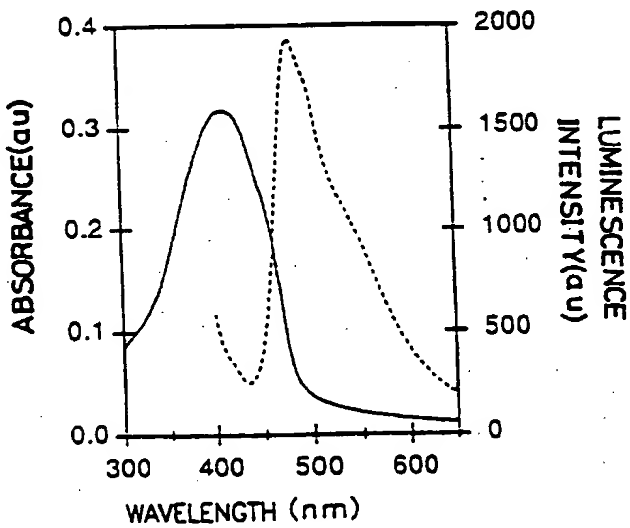

0.4
0.3
0.2
0.1
0.0
ABSORBANCE(au)
2000
1500
1000
500
0
LUMINESCENCE INTENSITY(au)
300
400
500
600
WAVELENGTH (nm)

FIG.3-7

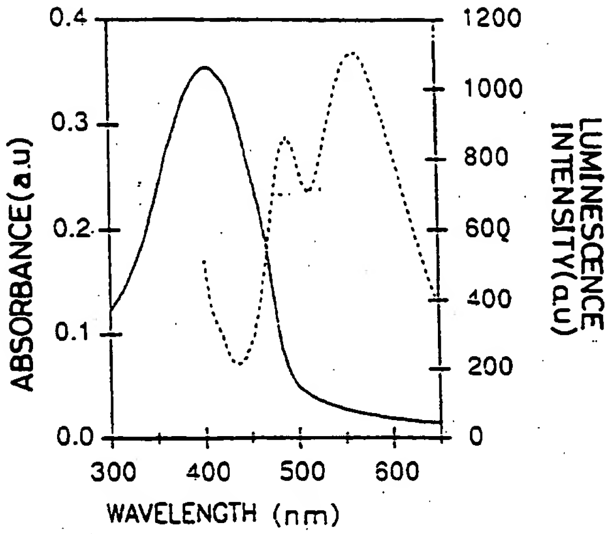

0.4
0.3
0.2
0.1
0.0
ABSORBANCE(a.u)
1200
1000
800
600
400
200
0
LUMINESCENCE INTENSITY(a.u)
300
400
500
600
WAVELENGTH (nm)

FIG.3-8

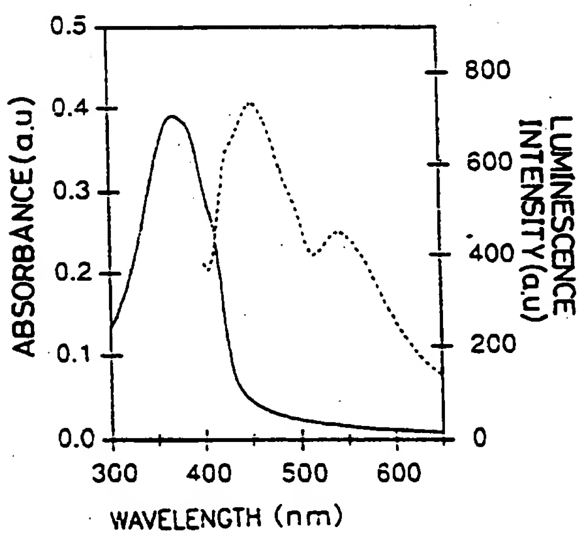

0.5
0.4
0.3
0.2
0.1
0.0
ABSORBANCE(a.u)
800
600
400
200
0
LUMINESCENCE INTENSITY(a.u)
300
400
500
600
WAVELENGTH (nm)

FIG.3-9

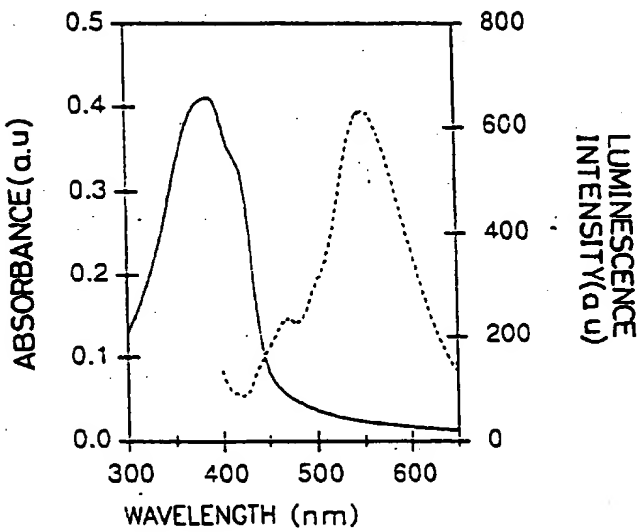


FIG.3-10

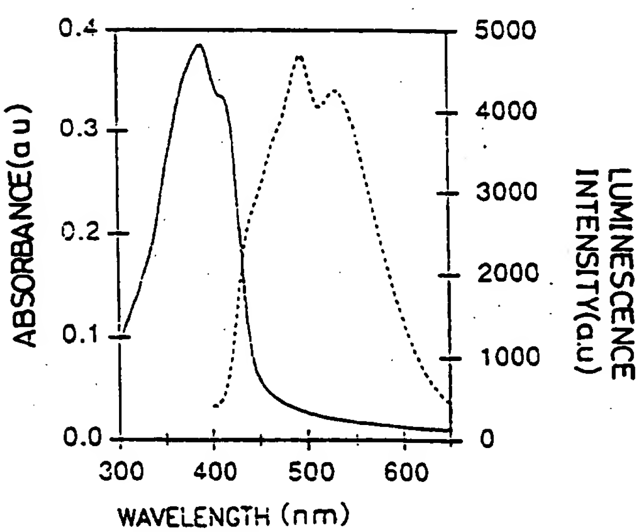


FIG.3-11

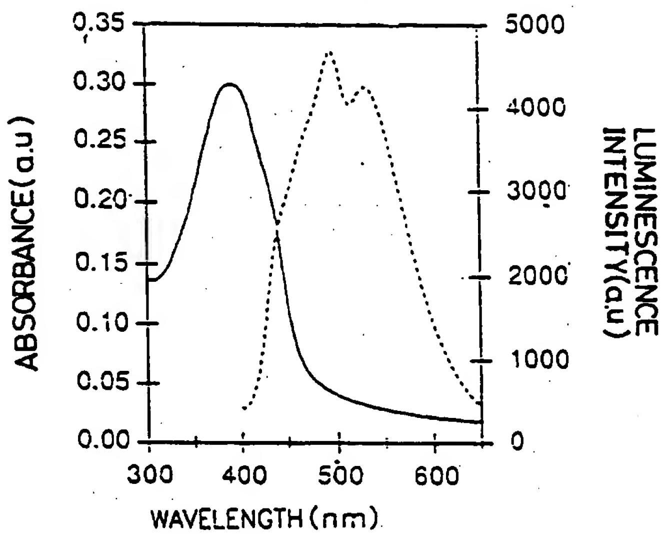


FIG.3-12

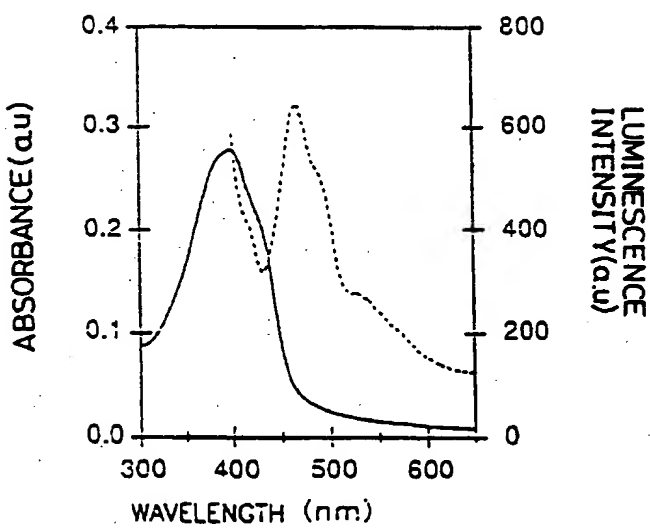


FIG.3-13

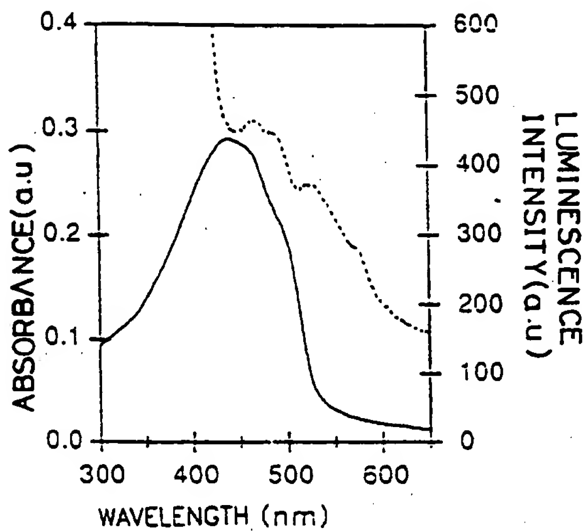


FIG.3-14

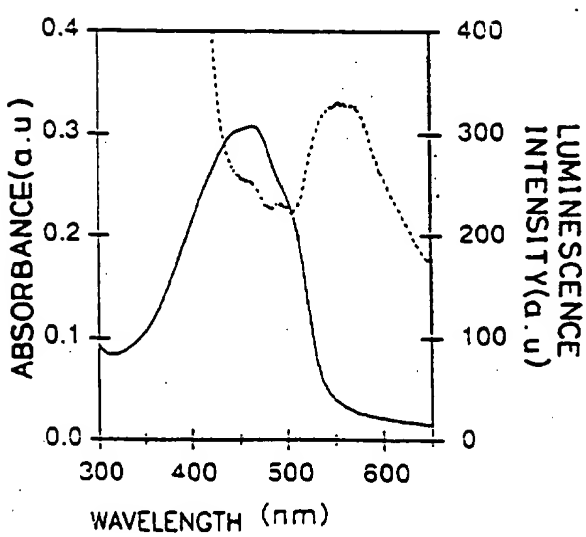


FIG.3-15

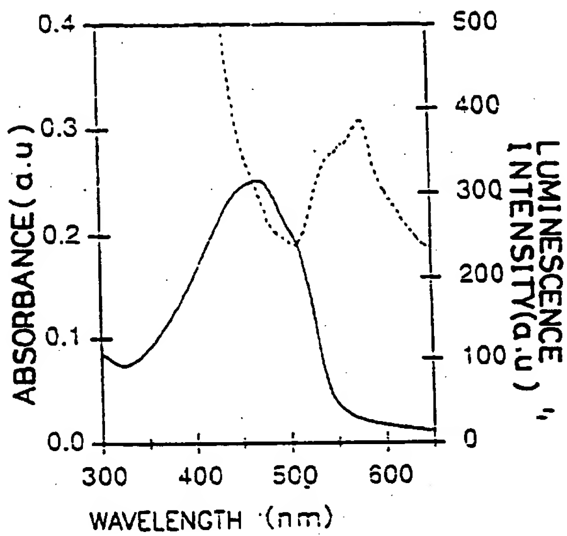


FIG.3-16

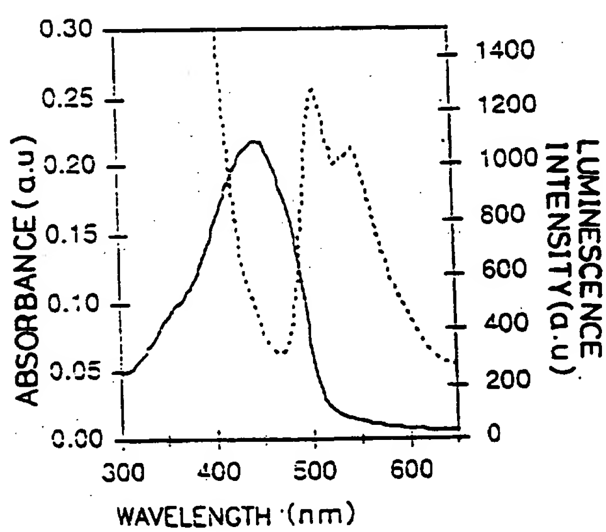


FIG.3-17

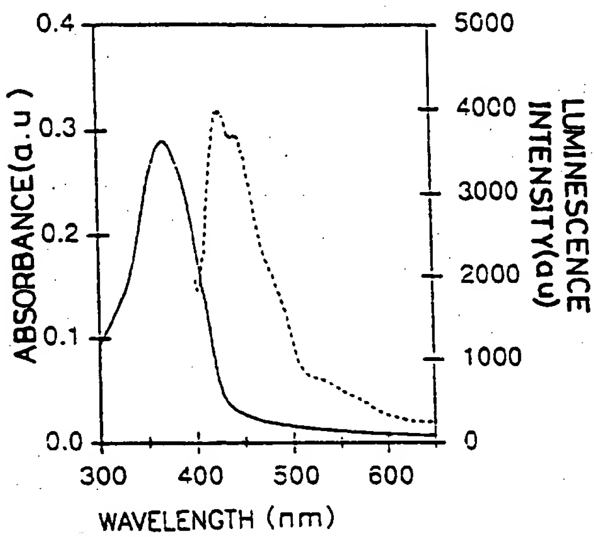


FIG.3-18

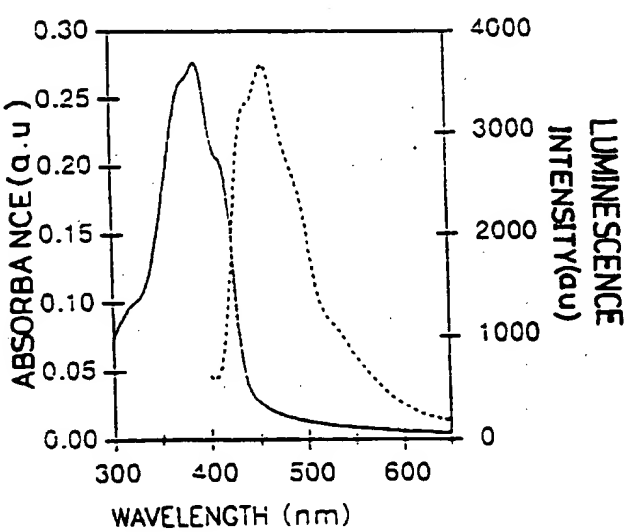


FIG.3-19

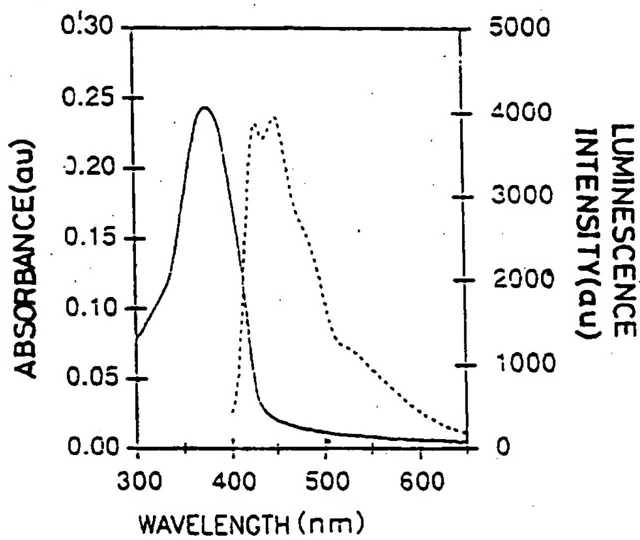


FIG.3-20

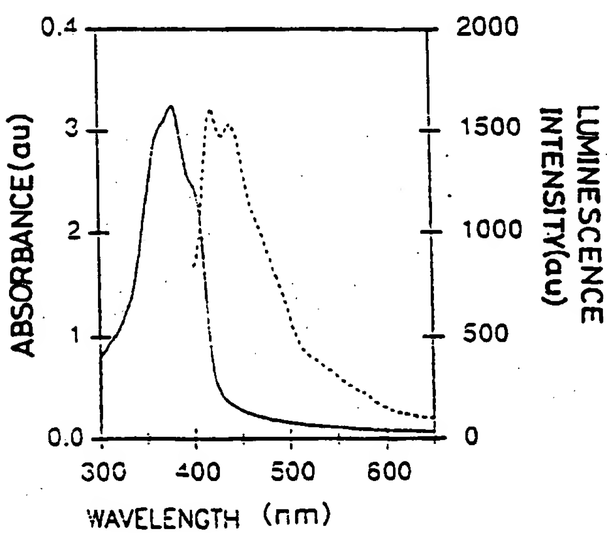


FIG.3-21

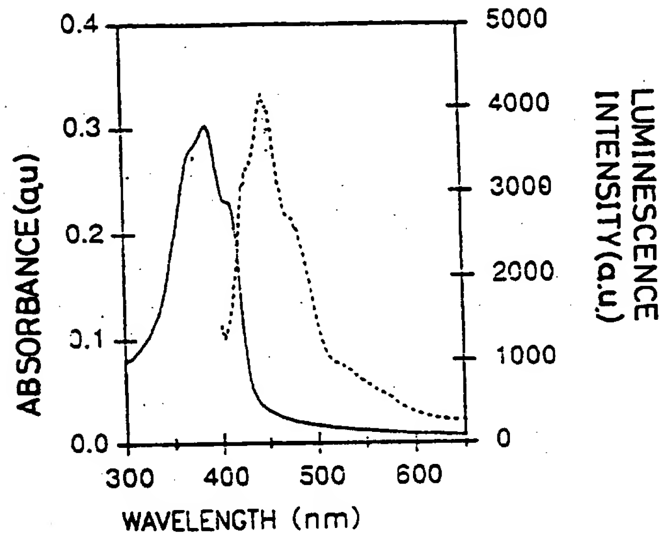


FIG. 4-1

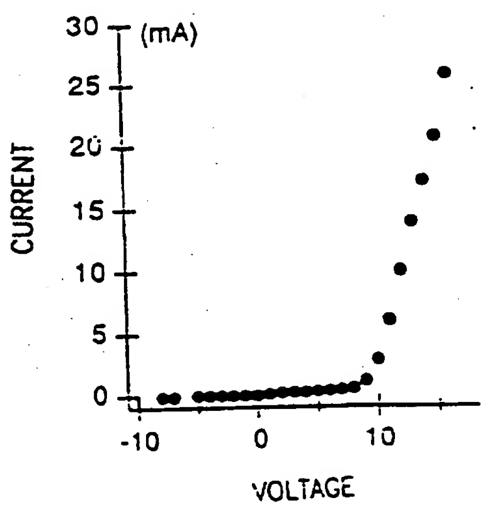


FIG. 4-2

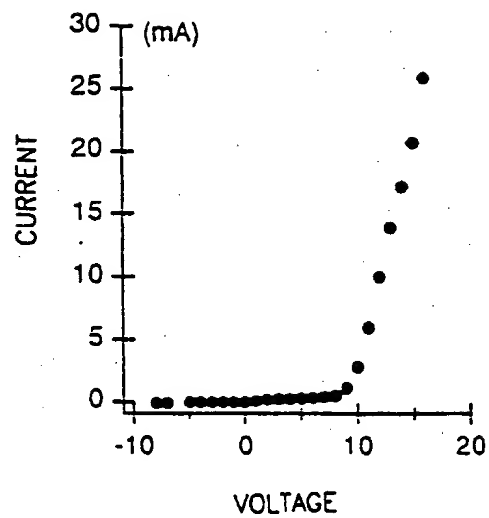

30
25
20
15
10
5
0
(mA)
CURRENT
-10
0
10
20
VOLTAGE

FIG. 4-3

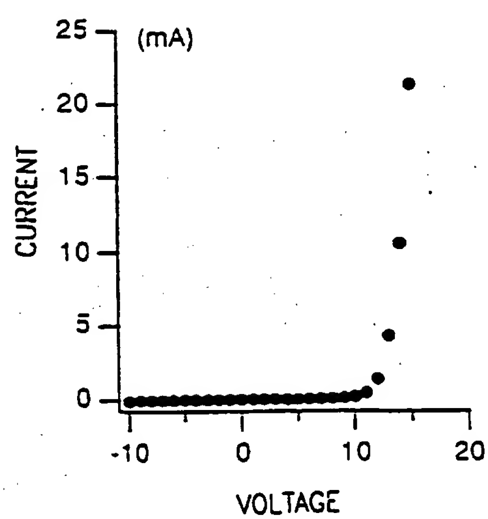

25
20
15
10
5
0
(mA)
CURRENT
-10
0
10
20
VOLTAGE

FIG. 4-4

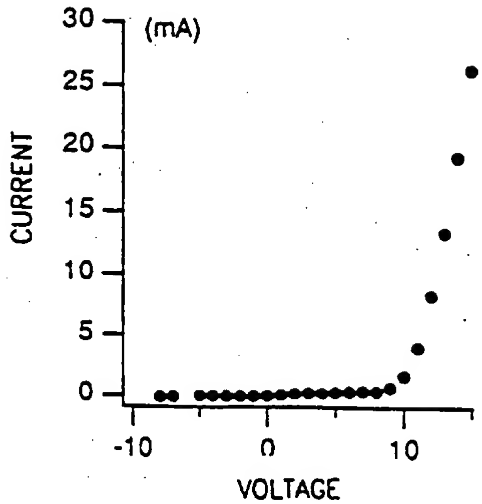

30
25
20
15
10
5
0
(mA)
CURRENT
-10
0
10
VOLTAGE

FIG. 4-5

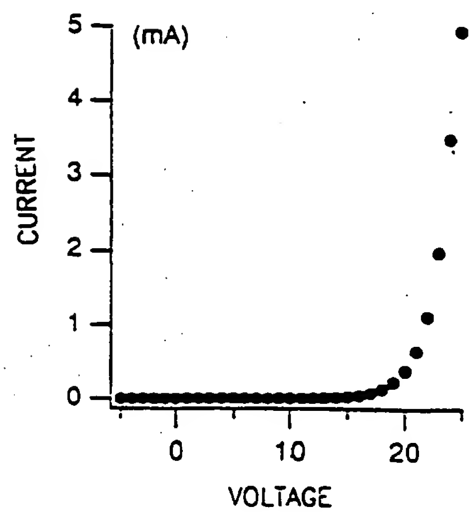

5
4
3
2
1
0
(mA)
CURRENT
0
10
20
VOLTAGE

FIG. 4-6

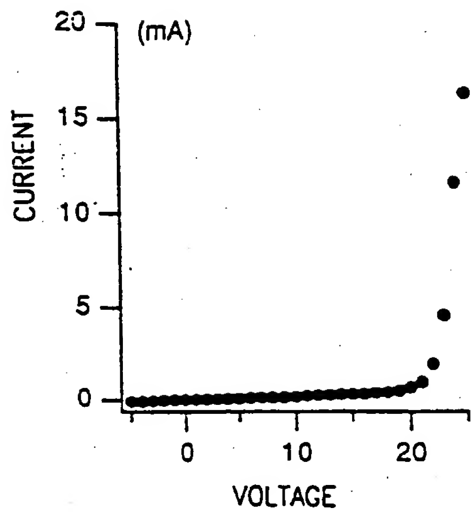

20
(mA)
15
10
5
0
CURRENT
0
10
20
VOLTAGE

FIG. 4-7

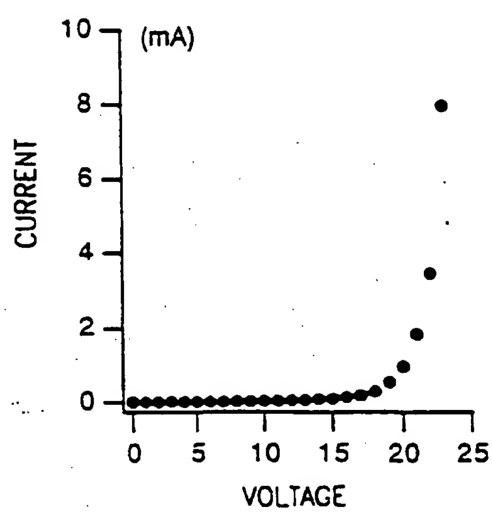

10
(mA)
8
6
4
2
0
CURRENT
0
5
10
15
20
25
VOLTAGE

FIG. 4-8

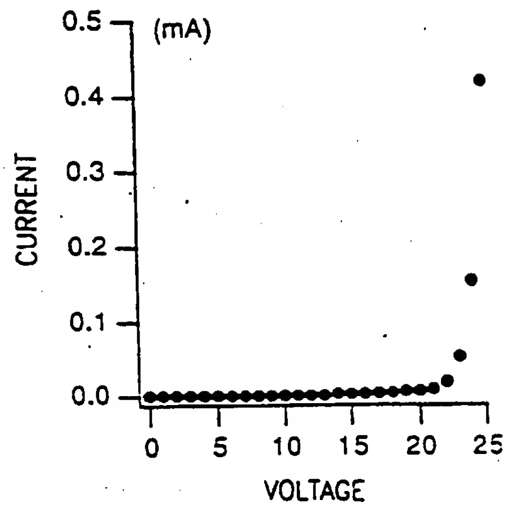

0.5
0.4
0.3
0.2
0.1
0.0
(mA)
CURRENT
0
5
10
15
20
25
VOLTAGE

FIG. 5-1

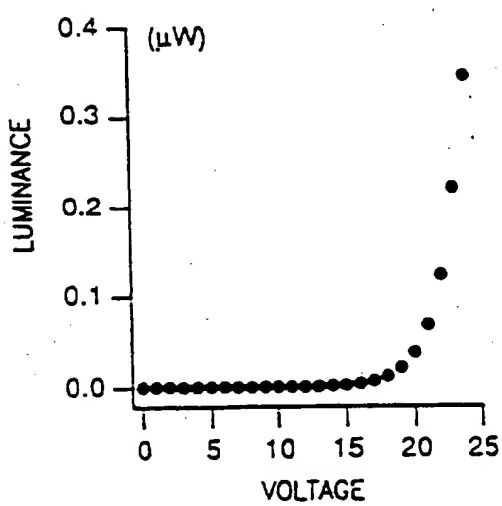

0.4
0.3
0.2
0.1
0.0
(μW)
LUMINANCE
0
5
10
15
20
25
VOLTAGE

FIG. 5-2

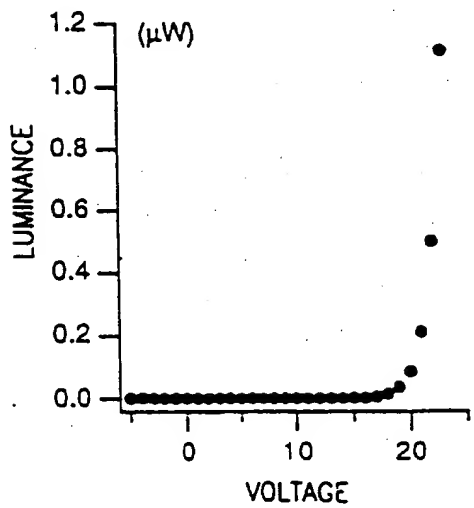

1.2
1.0
0.8
0.6
0.4
0.2
0.0
(μW)
LUMINANCE
0
10
20
VOLTAGE

FIG. 5-3

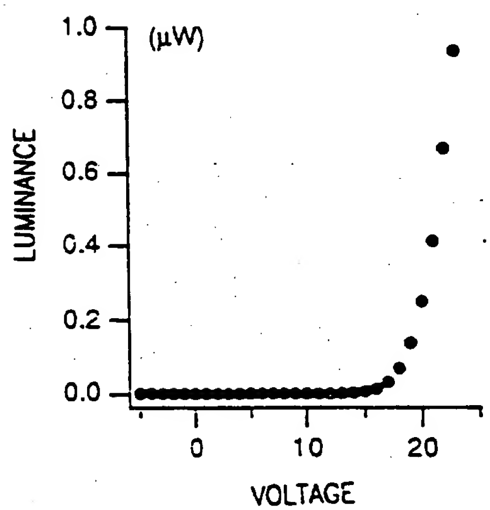

1.0
0.8
0.6
0.4
0.2
0.0
(μW)
LUMINANCE
0
10
20
VOLTAGE

FIG. 5-4

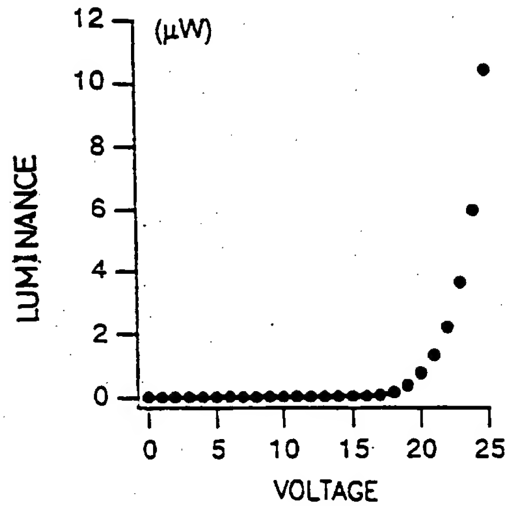

12
10
8
6
4
2
0
(μW)
LUMINANCE
0
5
10
15
20
25
VOLTAGE

FIG. 6-1

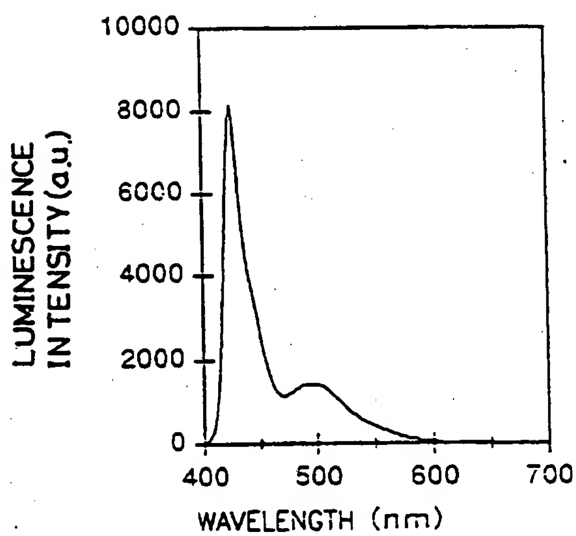

10000
8000
6000
4000
2000
0
LUMINESCENCE INTENSITY(a.u.)
400
500
600
700
WAVELENGTH (nm)

FIG. 6-2

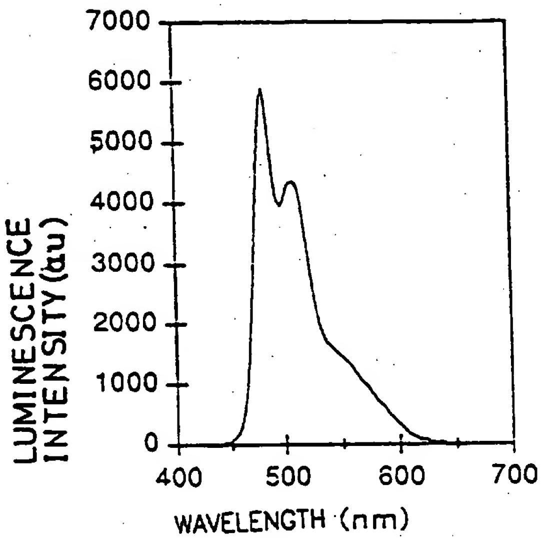

7000
6000
5000
4000
3000
2000
1000
0
LUMINESCENCE INTENSITY (a.u)
400
500
600
700
WAVELENGTH (nm)

FIG. 6-3

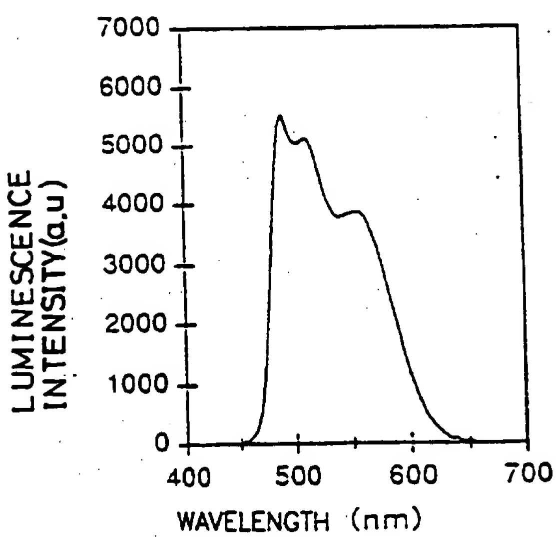

7000
6000
5000
4000
3000
2000
1000
0
LUMINESCENCE INTENSITY(a.u)
400
500
600
700
WAVELENGTH (nm)

FIG. 6-4

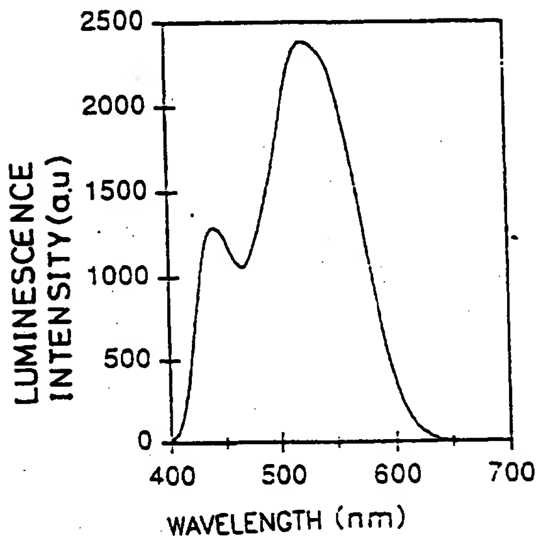

2500
2000
1500
1000
500
0
LUMINESCENCE INTENSITY(a.u)
400
500
600
700
WAVELENGTH (nm)

FIG. 7-1

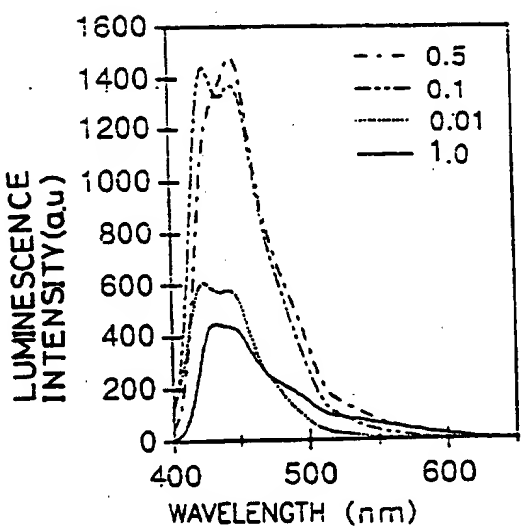

1600
1400
1200
1000
800
600
400
200
0
0.5
0.1
0.01
1.0
LUMINESCENCE INTENSITY(a.u)
400
500
600
WAVELENGTH (nm)

FIG. 7-2

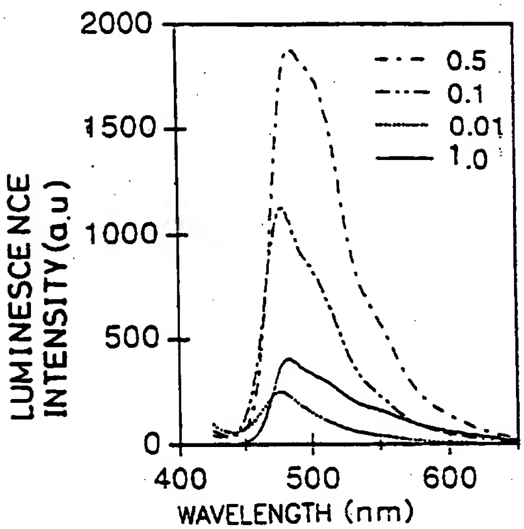

2000
1500
1000
500
0
400
500
600
WAVELENGTH (nm)
LUMINESCENCE INTENSITY(a.u)
0.5
0.1
0.01
1.0

FIG. 7-3

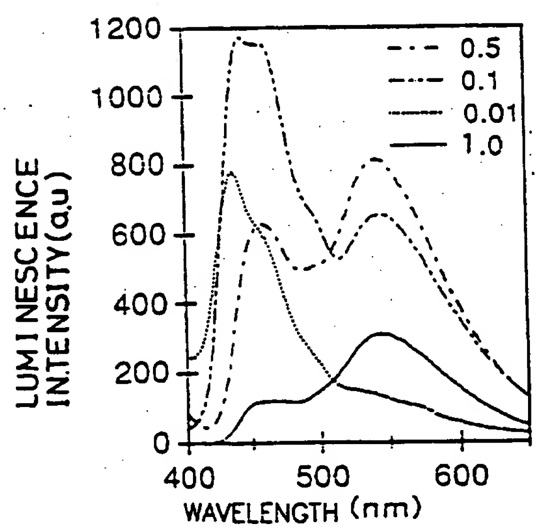
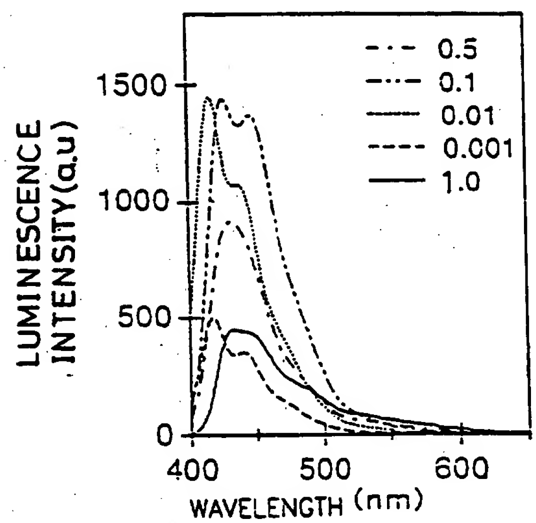
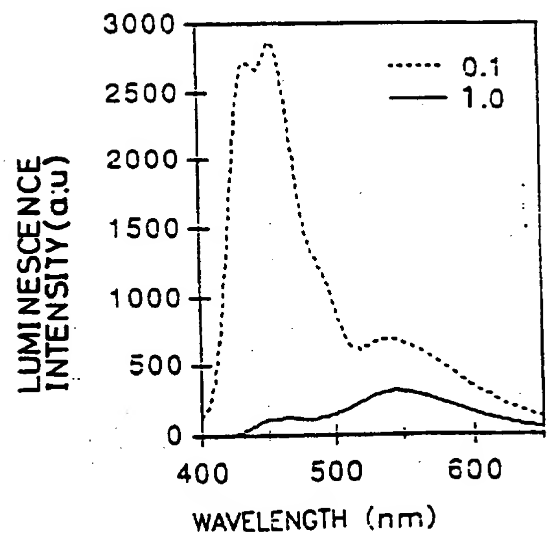

1200
1000
800
600
400
200
0
400
500
600
WAVELENGTH (nm)
LUMINESCENCE INTENSITY(a.u)
0.5
0.1
0.01
1.0

FIG. 7-4



0.5
0.1
0.01
0.001
1.0
1500
1000
500
0
400
500
600
LUMINESCENCE INTENSITY(a.u)
WAVELENGTH (nm)

FIG. 7-5



3000
2500
2000
1500
1000
500
0
0.1
1.0
400
500
600
LUMINESCENCE INTENSITY(a.u)
WAVELENGTH (nm)

FIG.7-6

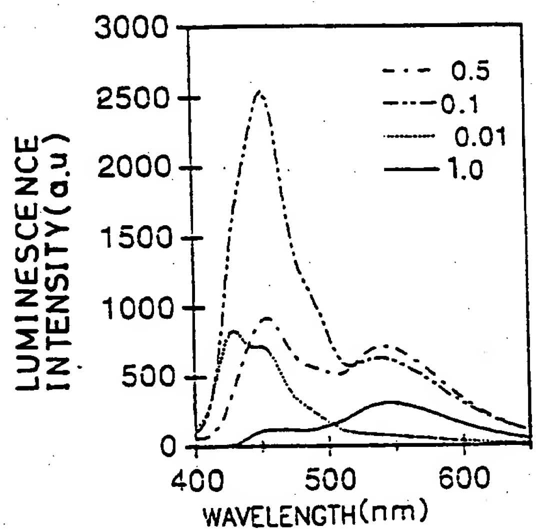

3000
2500
2000
1500
1000
500
0
LUMINESCENCE INTENSITY(a.u)
400
500
600
WAVELENGTH(nm)
0.5
0.1
0.01
1.0

FIG.7-7

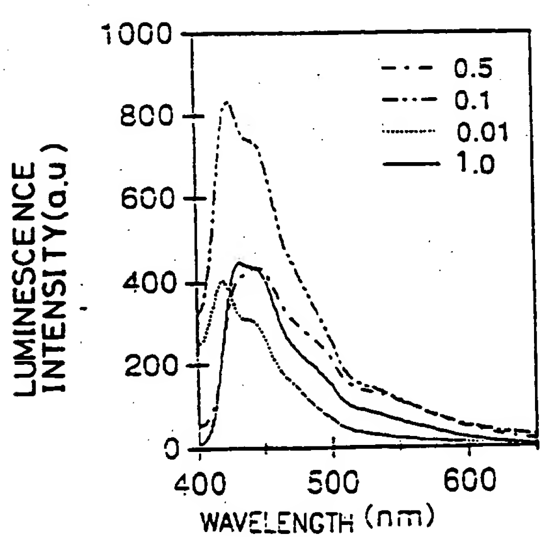

1000
800
600
400
200
0
LUMINESCENCE INTENSITY(a.u)
400
500
600
WAVELENGTH (nm)
0.5
0.1
0.01
1.0

FIG. 8-1

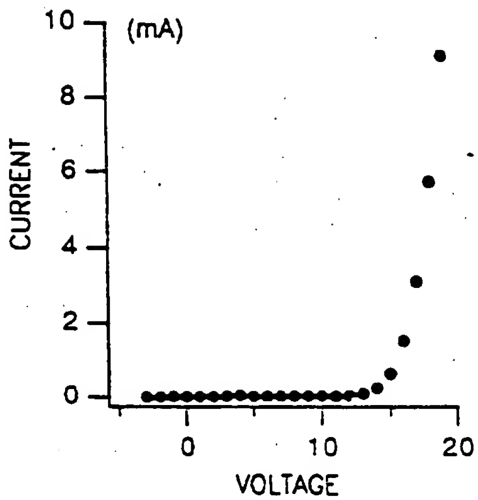

10
8
6
4
2
0
(mA)
CURRENT
0
10
20
VOLTAGE

FIG. 8-2

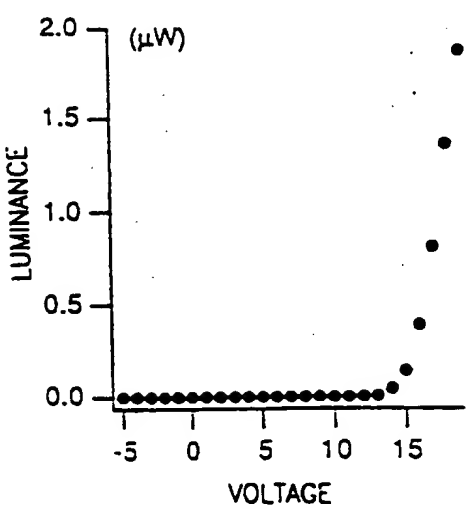
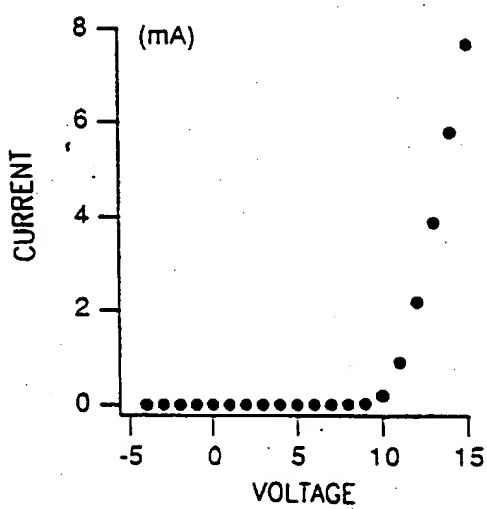
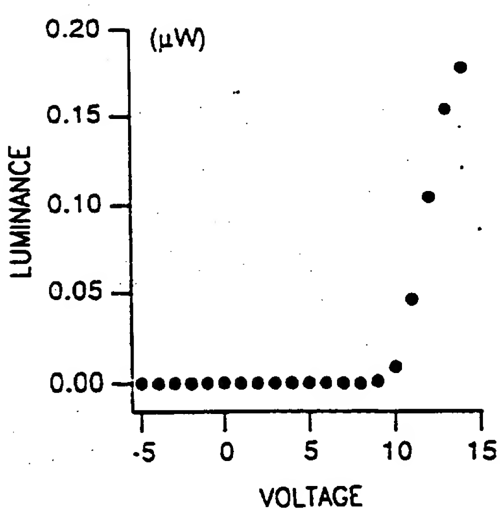

2.0
1.5
1.0
0.5
0.0
(μW)
LUMINANCE
-5
0
5
10
15
VOLTAGE

FIG. 8-3



(mA)
CURRENT
8
6
4
2
0
-5
0
5
10
15
VOLTAGE

FIG. 8-4



(μW)
LUMINANCE
0.20
0.15
0.10
0.05
0.00
-5
0
5
10
15
VOLTAGE

FIG. 8-5

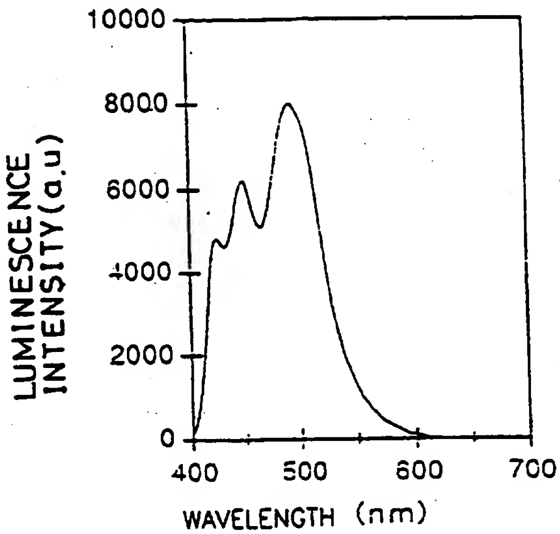

10000
8000
6000
4000
2000
0
LUMINESCENCE INTENSITY(a.u)
400
500
600
700
WAVELENGTH (nm)

FIG. 8-6

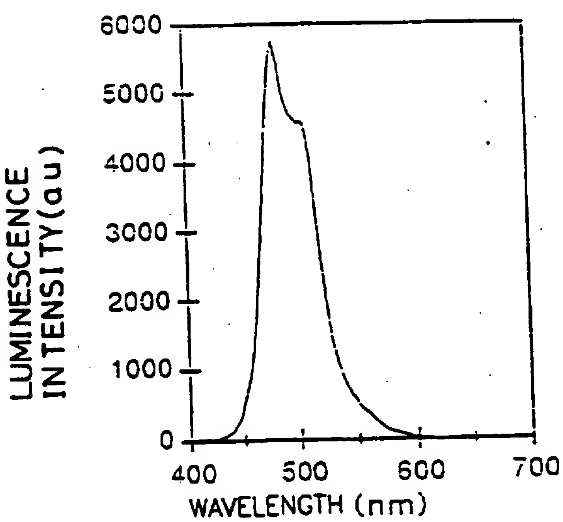
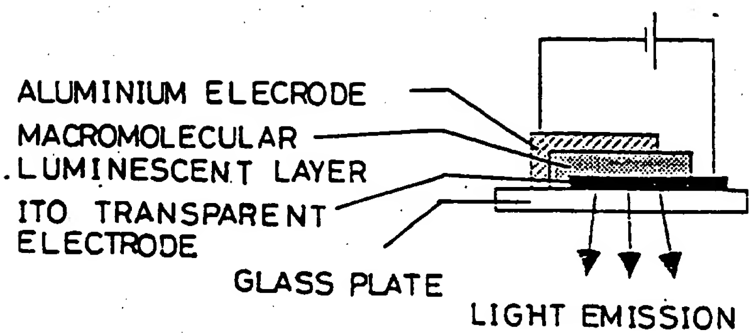

6000
5000
4000
3000
2000
1000
0
LUMINESCENCE INTENSITY(a.u)
400
500
600
700
WAVELENGTH (nm)

FIG. 9


ALUMINIUM ELECRODE
MACROMOLECULAR
LUMINESCENT LAYER
ITO TRANSPARENT
ELECTRODE
GLASS PLATE
LIGHT EMISSION

2313127

Fluorene-based Alternating Copolymers for Electroluminescence Element and Electroluminescence Element using such Copolymers as Light Emitting Materials

The present invention relates to fluorene-based alternating copolymers to be used as luminescent materials in manufacturing macromolecular electroluminescence (EL) elements, and relates to EL elements using such fluorene-based alternating copolymers as light emitting materials.

Examples of EL elements which have been studied thus far, include inorganic semiconductors such as GaAs which have the advantages of being small in size, require little consumption of electric power, etc., are currently being used as display devices having a small surface area, light emitting diode (LED) lamps, semiconductor lasers, and the like. However, in manufacturing such elements, extremely clean processing is required, and it is difficult to make LEDs of large surface area and it is difficult to obtain blue light having good efficiency. Furthermore, there are inorganic semiconductors having fluorescent ions of metal compounds added thereto, and inorganic EL elements made by

dispersing inorganic semiconductors into high molecules, but these cause problems in semiconductor stability not only because they require a high operating voltage but also because they operate under high electric fields.

However, as organic EL materials (Appl. Phys. Lett., 51, p.913 (1987)) and macromolecular EL materials (Nature, 347, p.539 (1990)) capable of overcoming such problems are recently being developed, advances in research in this field are continuing to progress. When voltage is applied to an EL element manufactured by depositing organic dyes (Japanese unexamined (laid-open) patent publications 6-136360 and 7-26254), or by putting macromolecules having a conjugate double bond (Int'l patents WO92/03491 and WO93/14177) between an anode and a cathode, holes from the cathode and electrons from the anode are introduced, move to a luminescent layer and emit light when they recombine thereafter. Currently, efforts are being made to find applications of such EL elements for next generation flat panel color display devices, electrochemical cells, image sensors, photocouplers, and the like which use LEDs, which will replace cathode-ray tubes, gas plasma displays, liquid crystal displays used at present. Elements manufactured by deposition of organic dyes have problems in reproducibility and in making uniform films, and macromolecule-based elements have overcome such problems to a certain degree, but improved stability, efficiency and durability are still required for desired applications to

practical commercial use. Poly(phenylene vinylene) (PPV), polythiophene (PTh) and polyphenylene-based macromolecules (Synth. Met.. 50(1-3), p.491 (1992) and Adv. Mater., 4, p. 36 (1992)), are known as representative macromolecular luminescent materials which have been studied up to now, but these materials have the disadvantage that the final material is insoluble in any organic solvent. The processing suitability is improved by introducing appropriate substituents and PPV or PTh derivatives (Synth. Met., 62, p.35 (1994), Adv. Mater., 4, p.36 (1994), and Macromolecules, 28, p. 7525 (1995)) which emit diverse lights of blue, green and red colors are known but the manufacturing process of such derivatives is very complicated, and there are also problems in stability. Moreover, fluorene-based macromolecules which emit blue light (Jpn. J. Appl. Phys., 30, p.L1941 (1991)) have been reported but these have disadvantages in that they can not exhibit various other colors, and require the use of materials and manufacturing methods from which macromolecules with more diversified conjugate double bonds can not be made.

Embodiments of the present invention will now be described by way of example only with reference to the accompanying drawings, in which:-

Fig. 1 shows ^{1}H-NMR spectrum of a polymer according to Example 11 of the present invention;

Fig. 2 shows ^{13}C-NMR spectrum of a polymer according to Example 11 of the present invention;

Fig. 3-1 shows the ultraviolet spectrum (—) and photoluminescence spectrum (---) of a polymer according to Example 1 of the present invention;

Fig. 3-2 shows the ultraviolet spectrum (—) and photoluminescence spectrum (---) of a polymer according to Example 2 of the present invention;

Fig. 3-3 shows the ultraviolet spectrum (—) and photoluminescence spectrum (---) of a polymer according to Example 3 of the present invention;

Fig. 3-4 shows the ultraviolet spectrum (—) and photoluminescence spectrum (---) of a polymer according to Example 5 of the present invention;

Fig. 3-5 shows the ultraviolet spectrum (—) and photoluminescence spectrum (---) of a polymer according to Example 6 of the present invention;

Fig. 3-6 shows the ultraviolet spectrum (—) and photoluminescence spectrum (---) of a polymer according to Example 7 of the present invention;

Fig. 3-7 shows the ultraviolet spectrum (—) and photoluminescence spectrum (---) of a polymer according to Example 8 of the present invention;

Fig. 3-8 shows the ultraviolet spectrum (—) and photoluminescence spectrum (---) of a polymer according to Example 10 of the present invention;

Fig. 3-9 shows the ultraviolet spectrum (—) and

photoluminescence spectrum (---) of a polymer according to Example 12 of the present invention;

Fig. 3-10 shows the ultraviolet spectrum (—) and photoluminescence spectrum (---) of a polymer according to Example 13 of the present invention;

Fig. 3-11 shows the ultraviolet spectrum (—) and photoluminescence spectrum (---) of a polymer according to Example 14 of the present invention;

Fig. 3-12 shows the ultraviolet spectrum (—) and photoluminescence spectrum (---) of a polymer according to Example 15 of the present invention;

Fig. 3-13 shows the ultraviolet spectrum (—) and photoluminescence spectrum (---) of a polymer according to Example 17 of the present invention;

Fig. 3-14 shows the ultraviolet spectrum (—) and photoluminescence spectrum (---) of a polymer according to Example 19 of the present invention;

Fig. 3-15 shows the ultraviolet spectrum (—) and photoluminescence spectrum (---) of a polymer according to Example 21 of the present invention;

Fig. 3-16 shows the ultraviolet spectrum (—) and photoluminescence spectrum (---) of a polymer according to Example 23 of the present invention;

Fig. 3-17 shows the ultraviolet spectrum (—) and photoluminescence spectrum (---) of a polymer according to

Example 24 of the present invention;

Fig. 3-18 shows the ultraviolet spectrum (—) and photoluminescence spectrum (---) of a polymer according to Example 25 of the present invention;

Fig. 3-19 shows the ultraviolet spectrum (—) and photoluminescence spectrum (---) of a polymer according to Example 26 of the present invention;

Fig. 3-20 shows the ultraviolet spectrum (—) and photoluminescence spectrum (---) of a polymer according to Example 27 of the present invention;

Fig. 3-21 shows the ultraviolet spectrum (—) and photoluminescence spectrum (---) of a polymer according to Example 28 of the present invention;

Fig. 4-1 shows the voltage-current characteristic curve of a polymer according to Example 1 of the present invention;

Fig. 4-2 shows the voltage-current characteristic curve of a polymer according to Example 2 of the present invention;

Fig. 4-3 shows the voltage-current characteristic curve of a polymer according to Example 3 of the present invention;

Fig. 4-4 shows the voltage-current characteristic curve of a polymer according to Example 5 of the present invention;

Fig. 4-5 shows the voltage-current characteristic curve of a polymer according to Example 6 of the present invention;

Fig. 4-6 shows the voltage-current characteristic curve of a polymer according to Example 7 of the present invention;

Fig. 4-7 shows the voltage-current characteristic curve of a polymer according to Example 8 of the present invention;

Fig. 4-8 shows the voltage-current characteristic curve of a polymer according to Example 10 of the present invention;

Fig. 5-1 shows the voltage-electroluminescence characteristic curve of a polymer according to Example 6 of the present invention;

Fig. 5-2 shows the voltage-electroluminescence characteristic curve of a polymer according to Example 7 of the present invention;

Fig. 5-3 shows the voltage-electroluminescence characteristic curve of a polymer according to Example 8 of the present invention;

Fig. 5-4 shows the voltage-electroluminescence characteristic curve of a polymer according to Example 10 of the present invention;

Fig. 6-1 shows the electroluminescent spectrum of a polymer according to Example 6 of the present invention;

Fig. 6-2 shows the electroluminescent spectrum of a polymer according to Example 7 of the present invention;

Fig. 6-3 shows the electroluminescent spectrum of a polymer according to Example 8 of the present invention;

Fig. 6-4 shows the electroluminescent spectrum of a polymer according to Example 10 of the present invention;

Fig. 7-1 shows the photoluminescence spectrum of a film

obtained by blending a polymer according to Example 6 of the present invention with polyvinylcarbazole (numbers in the box represents the weight fraction of the polymer);

Fig. 7-2 shows the photoluminescence spectrum of a film obtained by blending a polymer according to Example 7 of the present invention with polyvinylcarbazole (number in the box represents the weight fraction of the polymer);

Fig. 7-3 shows the photoluminescence spectrum of a film obtained by blending a polymer according to Example 12 of the present invention with polyvinylcarbazole (number in the box represents the weight fraction of the polymer);

Fig. 7-4 shows the photoluminescence spectrum of a film obtained by blending a polymer according to Example 6 of the present invention with polymethylmethacrylate (number in the box represents the weight fraction of the polymer);

Fig. 7-5 shows the photoluminescence spectrum of a film obtained by blending a polymer according to Example 12 of the present invention with polystyrene (number in the box represents the weight fraction of the polymer);

Fig. 7-6 shows the photoluminescence spectrum of a film obtained by blending a polymer according to Example 12 of the present invention with polymethylmethacrylate (number in the box represents the weight fraction of the polymer);

Fig. 7-7 shows the photoluminescence spectrum of a film obtained by blending a polymer according to Example 6 of the

present invention with epoxy (number in the box represents the weight fraction of the polymer);

Fig. 8-1 shows the voltage-current characteristics of a film obtained by blending a polymer (0.25 weight fraction) according to Example 6 of the present invention with polyvinylcarbazole;

Fig. 8-2 shows the voltage-electroluminescence characteristics of a film obtained by blending a polymer (0.25 weight fraction) according to Example 6 of the present invention with polyvinylcarbazole;

Fig. 8-3 shows the voltage-current characteristics of a film obtained by blending a polymer (0.5 weight fraction) according to Example 13 of the present invention with polyvinylcarbazole;

Fig. 8-4 shows the voltage-electroluminescence characteristics of a film obtained by blending a polymer (0.5 weight fraction) according to Example 13 of the present invention with polyvinylcarbazole;

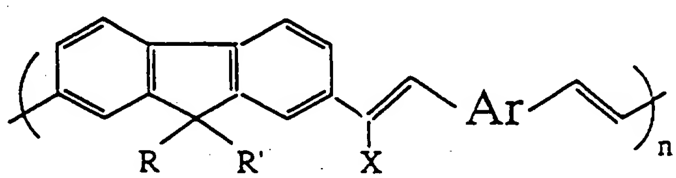
Fig. 8-5 shows the electroluminescent spectrum of a film obtained by blending a polymer (0.2 weight fraction) according to Example 6 of the present invention with polyvinylcarbazole;

Fig. 8-6 shows the electroluminescence characteristics of a film obtained by blending a polymer (0.2 weight fraction) according to Example 7 of the present invention with polyvinylcarbazole; and Fig. 9 shows the constitution of an embodiment of the electroluminescent element using as luminescent layer the fluorene-based alternating copolymer or blend of the

fluorene-based alternating copolymer and macromolecules for general use.

The present inventors have created the present invention as a result of their research for manufacturing diverse kinds of macromolecular EL materials which require only a simple manufacturing method, whereby the structure of the final substance is distinct, and being well soluble in any organic solvent.

For manufacturing the macromolecular EL elements according to the present invention, fluorene-based alternating copolymers having the following formula (I) is provided for use as a light emitting material:



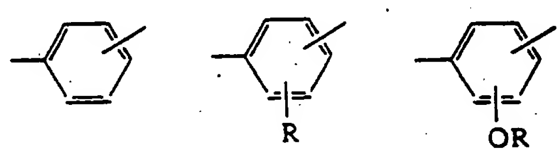
(I)

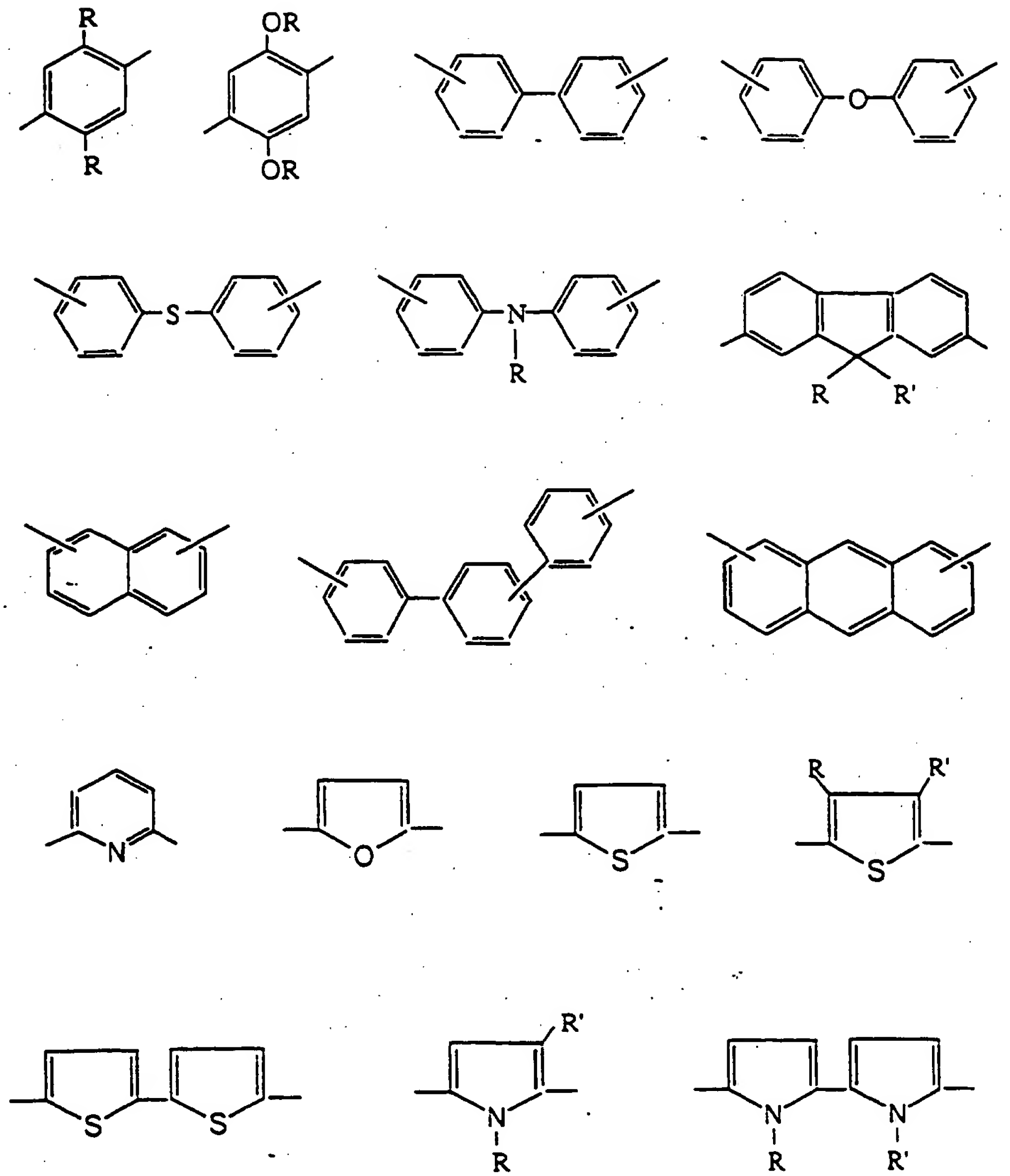
where R and R′ may be identical or different, and represent a hydrogen, an aliphatic or alicyclic alkyl or alkoxy group containing 1 to 22 hydrogens or carbons, or an aryl or aryloxy group containing 6 to 18 carbons. For example, R or R′ may represent hydrogen, methyl, ethyl, propyl, isopropyl, butyl, isobutyl, pentyl, hexyl, ethylhexyl, heptyl, octyl, nonyl, decyl,

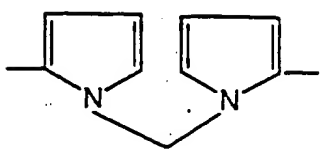
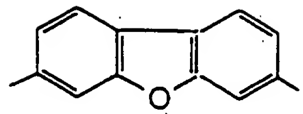
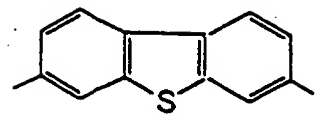
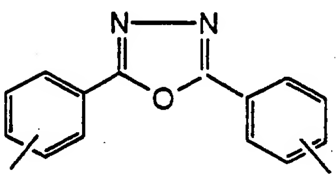
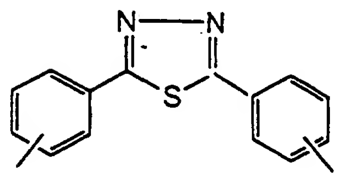
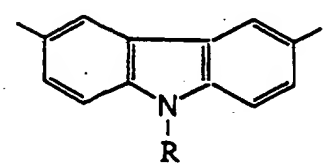
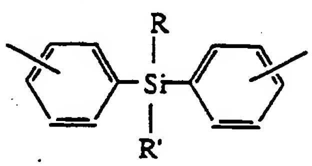
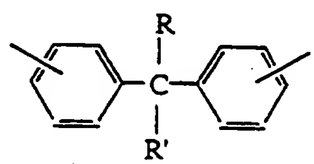
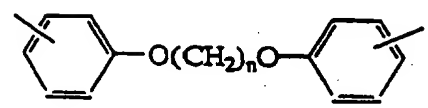
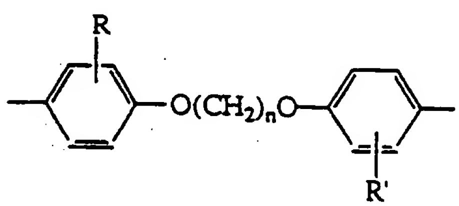
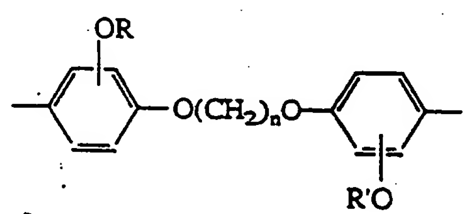
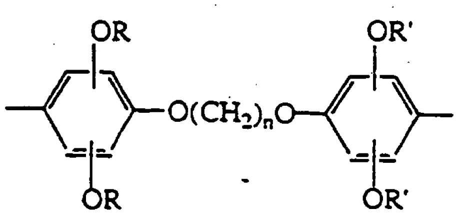
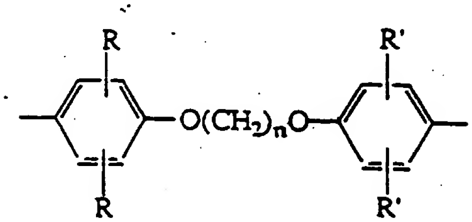
dodecyl, hexadecyl, octadecyl, docodecyl, cyclopropyl, cyclopentyl, cyclohexyl, ethoxy, buthoxy, hexyloxy, methoxyethoxyethyl, methoxyethoxyethoxyethyl, phenyl, phenoxy, tolyl, benzyl, naphthyl, anthracene group, etc.; X may represent hydrogen or cyano group; Ar may represent a compound substituted for aliphatic or alicyclic alkyl or an alkoxy group containing 1 to 22 carbons, phenyl groups in ortho-, meta-, para-positions, aliphatic or alicyclic alkyl or an alkoxy group containing 1 to 22 of carbons, such as dialkyl and a dialkoxypenyl group, compounds of diphenyl, diphenylether, diphenylsulfide, and diphenylamine of various isomers, compounds having two or more phenyl groups, such as fluorene, terphenyl, naphthalene, anthracene, and derivatives thereof, compounds having hetero atoms, such as pyridine, furan, thiophene, alkylthiophene, dithiophene, pyrrole, dipyrrole, dipyrrolemethane, dibenzofuran, dibenzothiophene, diphenyloxadiazole, diphenylthiadiazole, carbazole, and derivatives thereof, compounds of diphenylmethane or diphenylsilane, and compounds of bisformylphenoxyalkanes or alkoxy of various isomers; and n represents an integer greater than or equal to 1.

For reference, the said Ar groups can be illustrated as follows:

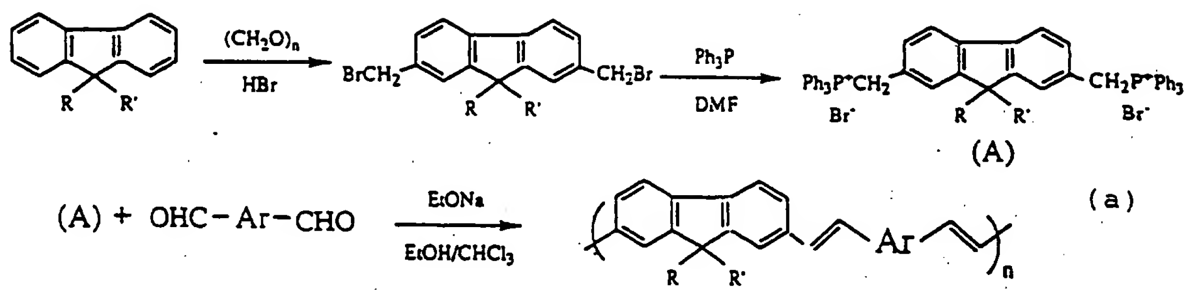
- Ar - = - (CH2)n -



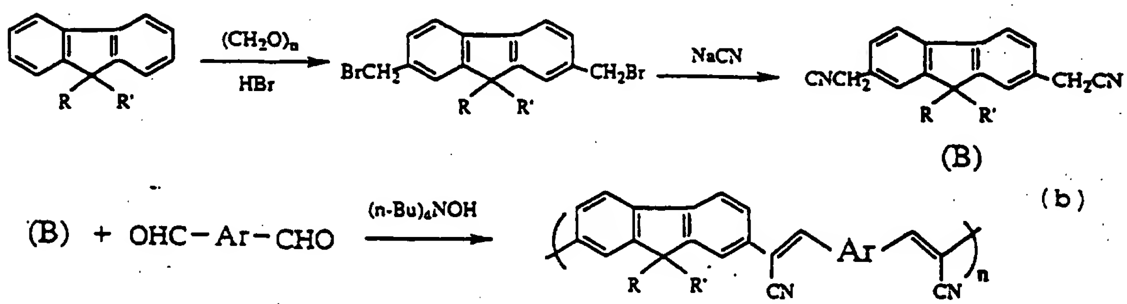


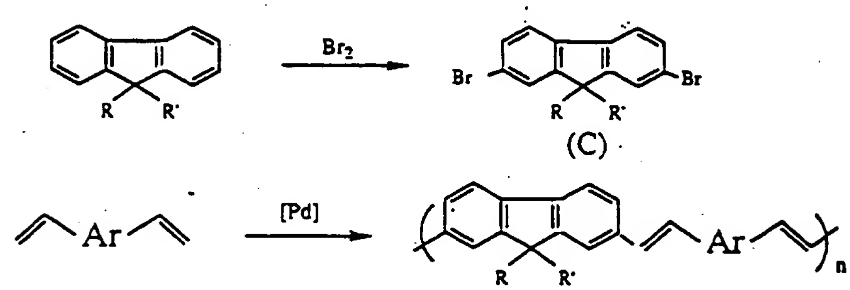
The polymerization degree and the manufacturing method of the polymers used in the present invention need not be particularly restricted. For instance, since such polymers are soluble in any organic solvent, the polymerization degree is generally 1 to 2,000, and preferably 3 to 1,000, to the extent that a film is formed by a spin coating or casting method. As examples of the manufacturing method of copolymers having conjugate double bonds, the present invention may employ known methods such as the Wittig reaction as shown in the following reaction formula (a) (J. Am. Chem. Soc., 82, p.4669, (1960), Org. React., 25, p.73, (1977)), the Knoevenagel condensation method as shown in the reaction formula (b) (J. Org. Chem., 25, p.813, (1960), Macromolecules, 27, p.3009, (1994)), the Heck reaction method by means of a palladium catalyst as shown in the reaction formula (c) (Org. React., 27, p.345, (1982), Macromolecules, 28, p.6410, (1995)), the method using a precursor as shown in the reaction formula (d) (U.S. Patent 3,401,152, J. Chem. Soc., Chem. Commun., p.32, (1992), Science, 269, p.376, (1995)), and the reaction using a strong base such as potassium-tert-butoxide as shown in the reaction formula (e) (J. Polym. Sci., Part A-1, 4, p.1337 (1966), Synth. Met., 62, p.35 (1994)).



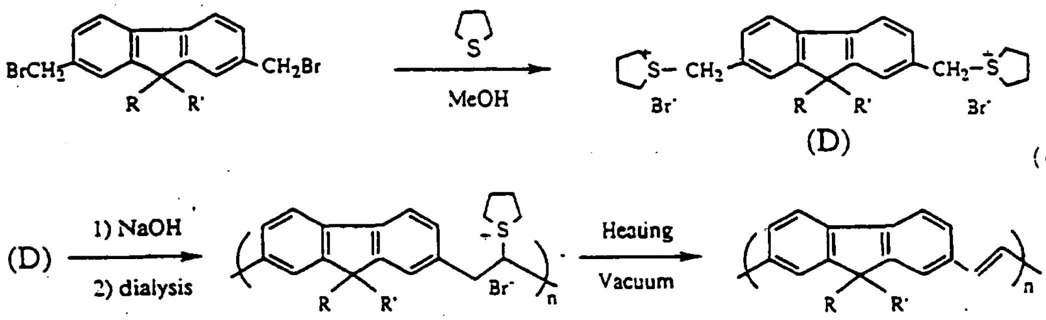
(a)



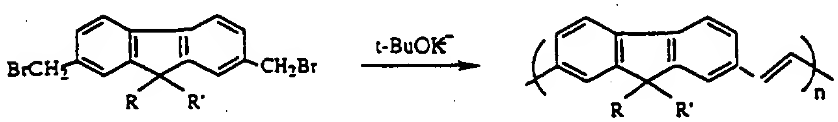
(b)



(c)



(d)



(e)

Explaining each formula in more detail, the monomers used in the Wittig polymerization are generally phosphonium salt and dicarboxaldehyde, which are reacted with a strong basic catalyst, such as sodium or alkyl lithium using an organic solvent, such as ethanol. According to the present invention, bis-bromo (or chloro) methyl fluorene phosphonium or fluorene-substituted phosphonium, and various dicarboxaldehydes may be used, whereby all fluorene-based phosphonium salts and all aliphatic, alicyclic and aromatic dicarboxaldehydes that are capable of formulating the formula (I) after polymerization are included. Specific examples of fluorene-based phosphonium salts include phosphonium salts having an aliphatic (or alicyclic) alkyl group or an aliphatic (or alicyclic) alkoxy group having 1 to 22 carbons in place of one hydrogen at the 9 position, or phosphonium salts

having an aryl or aryloxy group having 6 to 18 carbons in place of one hydrogen at the 9 position, for example, 2,7-bis (bromomethyl) fluorene triphenyl phosphonium salt or 2,7 bis (bromomethyl)-9-alkyl (alkoxy or aryl) fluorene triphenyl phosphonium salt; and phosphonium salts having an aliphatic (or alicyclic) alkyl group or an aliphatic (or alicyclic) alkoxy group having 1 to 22 carbons in place of two hydrogens at the 9 position, or phosphonium salts having an aryl or aryloxy group having 6 to 18 carbons in place of two hydrogens at the 9 position, for example, 2,7-bis (bromomethyl)-9,9'-dialkyl (alkoxy or aryl) fluorene triphenyl phosphonium salts.

Dicarboxaldehydes include, aliphatic dicarboxaldehydes such as glutaldehyde; unsubstituted aromatic discarboxaldehydes such as phthaldehyde, isophthaldehyde, and terephthaldehyde; aromatic dicarboxaldehydes having an aliphatic (or alicyclic) alkyl group or an aliphatic (or alicyclic) alkoxy group having 1 to 22 carbons, or having an aryl or aryloxy group having 6 to 18 carbons, such as 1,4-dialkyl (alkoxy or aryl) phenyl-2,5-dicarboxaldehyde; diformyl diphenyl derivatives, 2,7-diformyl fluorene derivatives, ortho- or metha- or para-terphenyl diformyl compounds, such as 2,2'- or 3,3'- or 4,4'-diphenyl dicarboxaldehyde or bis(2-or 3-or 4-formyl phenyl)ether or sulfide or alkylamine; naphthalene dicarboxaldehyde compounds such as 1,8- or 2,6-naphthalene dicarboxaldehyde; anthracene dicarboxaldehyde compounds such as

1,8- or 9,10-anthracene dicarboxaldehyde; 2,6-pyridine dicarboxaldehyde, 2,5-furane dicarboxaldehyde, 2,5-thiophene dicarboxaldehyde, 5,5'-diformyl-2,2'-dithiophene, 3-alkyl-2,5-thiophene dicarboxaldehyde, 2,5-pyrrole dicarboxaldehyde, N,N'-dipyrrole methane-2,2'-dicarboxaldehyde, 2,8-dibenzofuran dicarboxaldehyde, 2,8-dibenzothiophene dicarboxaldehyde, 2,5-bis(2-or 3-or 4-formylphenyl)-1,3,4-diphenyl thiadiazole, and diformylcarbazoles substituted with aliphatic or alicyclic alkyl group having 1 to 22 carbons, such as N-alkyl-3,6-diformylcarbazole.

Monomers used in the Knoevenagel condensation method related to the present invention are bis(bromomethyl) fluorene and its derivatives and dicarboxaldehyde compounds. In lieu of bis(bromomethyl) fluorene and its derivatives, bis(cyanomethyl) fluorene and its derivatives obtained by reaction with cyanide compounds such as sodium cyanide can be used, and the dicarboxaldehyde compounds of the Wittig polymerization can also be used as is in the present invention. The polymerization is carried out by reacting these two compounds using an organic solvent such as tetrahydrofuran or toluene, in the presence of a strong basic catalyst, such as tetrabutylammonium hydroxide or potassium-tert-butoxide.

In the Heck reaction method using a palladium catalyst, aromatic dibromide or diiodide and divinyl compounds are subject

to a condensation reaction together with amine compounds such as palladium acetate, tri-o-tolylphosphine and tributylamine, in the presence of a basic solvent such as dimethylformamide. Thus, dibromide or diiodide derivatives obtained by adding brome or iodic acid to the said fluorene derivatives may be used as aromatic dibromide or diiodide compounds related to the present invention. For example, if fluorene or 9-alkyl or 9,9'-dialkyl fluorene is treated with bromine in the presence of dimethylformamide or chloroform solvent, 2,7-dibromo fluorene or an alkyl group substituted fluorene compound may be obtained. The aromatic divinyl compound may be obtained by subjecting the dicarboxaldehyde compounds such as metha-divinylbenzene, para-divinylbenzene, 2,2'- or 3,3'- or 4,4'-divinyl diphenyl, 2,5-divinyl thiophen, 2,6-divinyl naphthalene, etc. to the Wittig reaction.

In connection with the present invention, a method using a precursor can be employed to easily obtain tetrahydrothiophene salt by reacting bis(chloro or bromomethyl) fluorene and its derivatives with tetrahydrothiophene in the presence of methanol. Consequently, the bis(chloro or bromomethyl) fluorene and its derivatives used in the Wittig polymerization may be used for the reaction as is. When the thusly obtained salts are polymerized in water or methanol solvent, and then dialyzed and heated in a vacuum, the polymer of the present invention can be obtained.

The polymers related to the present invention can be easily

obtained by reacting the bis(chloro or bromomethyl) fluorene and its derivatives with a strong base such as potassium-tert-butoxide or normal-butyllithium, in the presence of toluene or tetrahydrofuran solvent. Accordingly, the bis(chloro or bromomethyl) fluorene and its derivatives may be used as a monomer.

The constitution of EL elements using fluorene-based macromolecules according to the present invention, includes a general element constitution in which the material of the present invention is inserted between an anode and a cathode, that is, an element constitution of anode / luminescent layer / cathode, and also can additionally use the known hole or electron transporting layer materials (Japanese unexamined (laid-open) patent applications 2-135361, 3-152184, 6-207170) and the possible element constitutions are not particularly limited. In other words, a constitution of anode/hole transporting layer / luminescent layer / electron transporting layer / cathode would also be included. An anode ordinarily comprise a transparent supporting substrate such as glass, transparent plastics, quartz, etc. with a metal or metal oxide such as ITO, gold, copper, tin oxide, zinc oxide, etc. as electrode materials or an organic semiconductor compound such as polypyrrole, polyaniline or polythiophene coated to a thickness of 10 nanometers to 1 micron thereon. A cathode is usually made of a metal such as sodium, magnesium, calcium, aluminum, indium, silver, gold, copper, etc.,

or alloy metals thereof. The hole transporting layer can be formed by coating with polyvinylcarbazole, 2,5-bis(4'-diethyl aminophenyl)-1,3,4-oxadiazole, N,N'-diphenyl-N,N'-(3-methyl phenyl)-1,1'-biphenyl-4,4'-diamine(TPD), etc., while the electron transporting layer can be formed with the known compounds such as tris (8-hydroxyquinolinato) aluminum, 2-(4'-tert-butylphenyl) -5-(4"-biphenyl)-1,3,4-oxadiazole, 2,4,7-trinitro-9-fluorenone, etc., employing known film formation methods, such as vacuum deposition, spin coating, casting, LB method, etc.

The luminescent polymers of the present invention can also be used by blending with the hole or electron transporting layers or other mutually different polymers of the present invention, and existing luminescent polymers such as soluble PPV or PTh derivatives. For instance, polyvinylcarbazole, poly(1,4-hexyloxy-2,5-phenylenevinylene)poly(3-hexylthiophene), etc. and the fluorene-based macromolecules of the present invention are dissolved in an organic solvent such as chloroform and then coated by spin coating, casting method, etc. Although no particular restrictions are required, it is desirable to use the fluorene-based macromolecules of the present invention in a concentration of more than 0.001 % by weight, preferably 0.1 to 50% by weight to polyvinylcarbazole, and the film in thickness of 5 nanometers to 5 microns, preferably 50 nanometers to 1 micron. Furthermore, macromolecules that are soluble in any general organic solvent and that are capable of forming into a film

structure even though such macromolecules do not form a hole or electron transporting layer, may be used by blending them in the same concentration and thickness mentioned above. Macromolecules which can be used include thermoplastics, such as polymethylmethacrylate, polyarcylate, polystyrene, polycarbonate, polyvinylchloride, polyethylene, polypropylene, polyacrylonitrile, polyvinylpyrrolidone, polyvinylalcohol, polyvinylacetate, polyvinylbutyral, polyvinylamine, polycaprolacton, polyethylentherephthalate, polybutylentherephthalate, polyurethan, ABS, polysulfone, polyvinylfluoride, etc., or resins for general use, such as acetal, polyamides, polyimides, polyester, alkyd, urea, furan, nylon, melamine, phenol, silicon, epoxy, etc.

The present invention is hereinafter described in details by examples which are not limitative.

Example:

Synthesis of monomers

Monomers to be used in the present invention are not required to be particularly restricted. For example, any monomer will do as long as the polymer formed after polymerization is a macromolecule satisfying the formula (I). Even though it is not specifically mentioned in the following descriptions, compounds that can be easily synthesized in general, that are already well known or which are similar, or monomers that are commercially